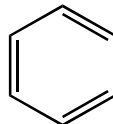
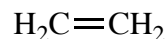
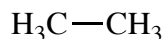


Lecture Notes
Chem 51B
S. King

Chapter 17 Benzene and Aromatic Compounds

I. The Structure of Benzene

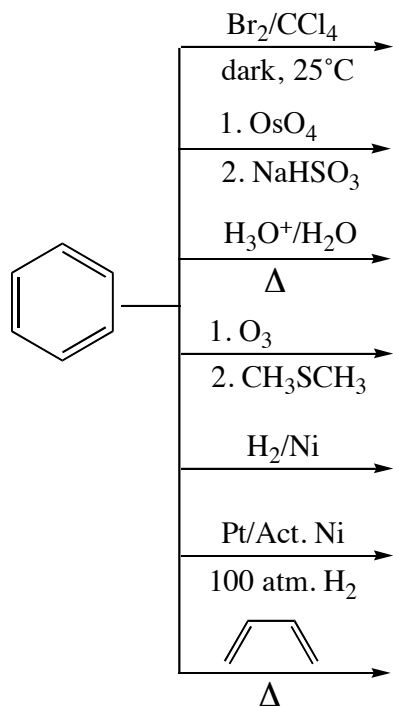
- In the resonance hybrid, the six electrons from the three π -bonds are delocalized over the entire ring.
- The dashed lines inside the hexagon in the resonance hybrid of benzene indicate that the π -electrons are delocalized and shared equally by all 6 C's.
- The dashed lines also indicate that all C–C bonds have the same length:



Hybridization and orbitals:

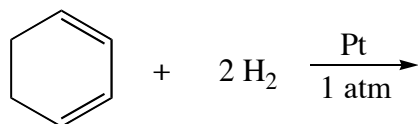
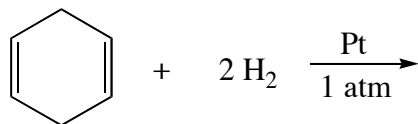
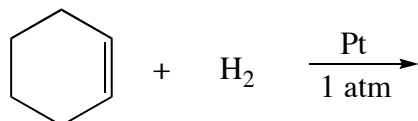
II. Aromaticity

Benzene is the simplest aromatic hydrocarbon. Aromatic compounds have unusual stability that goes far beyond what is predicted by simple resonance stabilization (it is unreactive in reactions that you would typically expect alkenes or conjugated dienes to undergo.)



Q. Is resonance stabilization alone adequate to explain the special stability of benzene?

A. To answer this question, let's predict the expected resonance stabilization for benzene, and compare this with the experimental resonance stabilization obtained when benzene is hydrogenated.



ΔH° for two isolated double bonds:

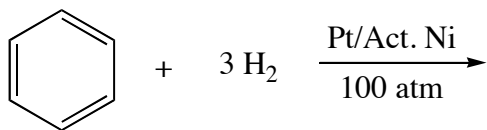
ΔH° for two conjugated double bonds:

The difference is the resonance energy!

\therefore Resonance energy for two conjugated double bonds:

Look @ Benzene:

if two conjugated double bonds have 1.8 kcal/mole resonance energy
then three conjugated double bonds should have:



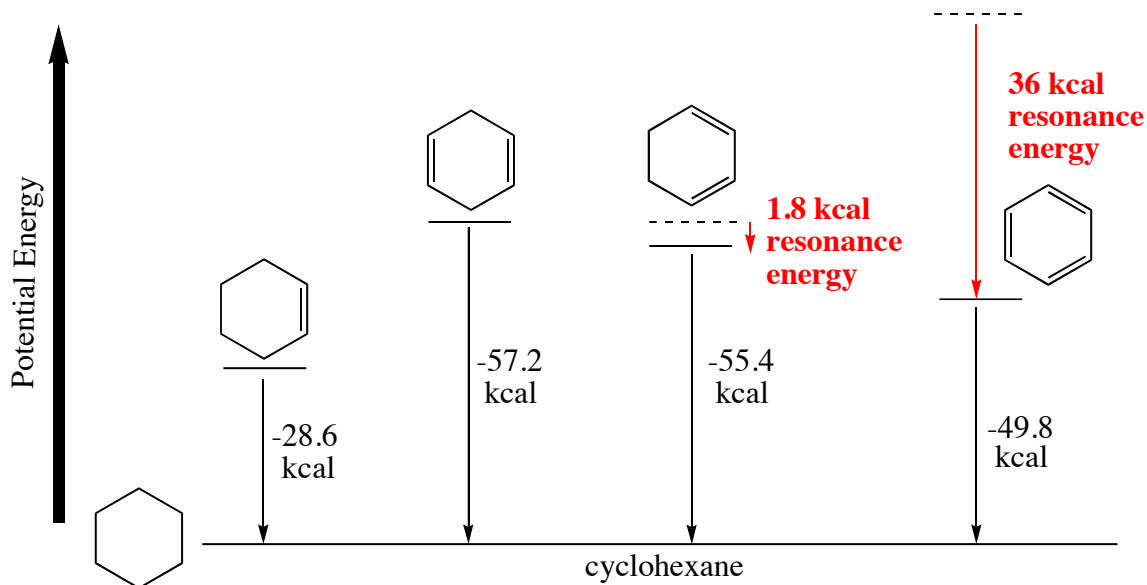
Expected ΔH° for three isolated double bonds:

Actual ΔH° for benzene (3 conjugated double bonds):

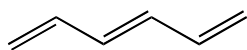
Actual resonance energy:

- This **HUGE** resonance energy cannot be explained by simple conjugation effects alone!

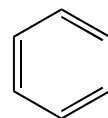
This can be shown graphically:



Compare:



vs.



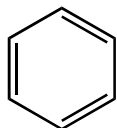
If resonance stabilization were the only reason for benzene's stability, we might also expect similar conjugated systems to also be unusually stable.

Q. Are similar conjugated systems unusually stable?

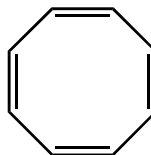
A. Look @ the following similar conjugated systems:



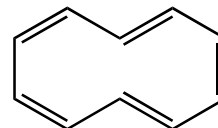
cyclobutadiene



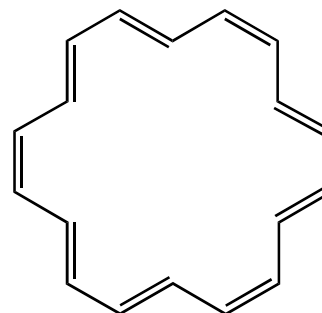
benzene



cyclooctatetraene



cyclodecapentaene



[18] annulene

Conclusion: There must be something more than typical resonance stabilization explain benzene's extraordinary stability!

The Molecular Orbital picture for benzene provides the explanation we are looking for.

☛ **To draw** MO picture for benzene, or any planar molecule with an uninterrupted cyclic π -electron cloud, use **Frost's circle**: Draw the cyclic compound with one of its vertices pointed down. The relative energies of the π -MO's correspond to the relative levels of the vertices. MO's below the midpoint are bonding MO's. MO's above the midpoint are antibonding MO's.

- This configuration, with all bonding M.O.'s filled (a closed bonding shell) is energetically very favorable, and accounts for the special stability associated with aromaticity.
- There are other numbers of electrons that correspond to filled shells for smaller & larger rings.

Hückel's Rule: Any *conjugated monocyclic polyene* that is *planar* and *has $(4n + 2)\pi$ electrons* with $n = 0, 1, 2, \dots$ etc. will exhibit the special stability associated with **aromaticity**. Systems with $(4n)\pi$ electrons are **antiaromatic** (less stable than the open chain counterpart.)

To be aromatic, a compound *must satisfy ALL four rules*:

1. Structure must be cyclic.
2. Each atom in the ring must have an unhybridized p-orbital.
3. The structure must be planar to allow for continuous overlap of parallel p-orbitals.
4. Delocalization of the π -electrons over the ring must result in a lowering of the electronic energy:

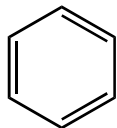
If $(4n + 2)\pi$ electrons: **aromatic**

If $4n \pi$ electrons: **antiaromatic**

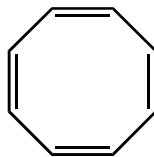
Look @ previous examples again:



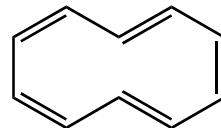
cyclobutadiene



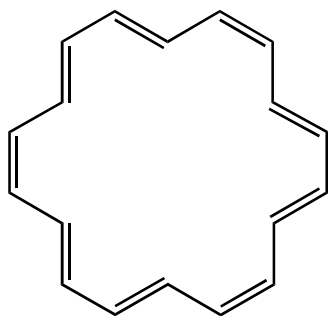
benzene



cyclooctatetraene

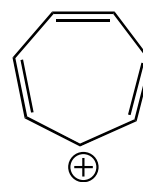
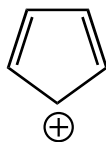
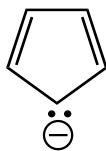


cyclodecapentaene

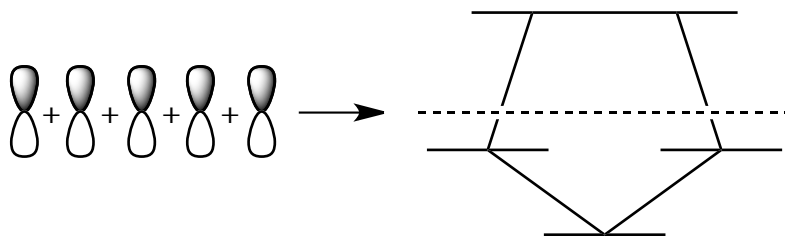
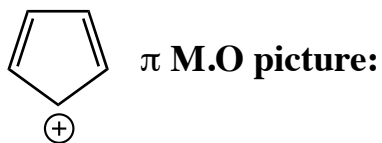


[18] annulene

Ionic cyclic polyenes can also be aromatic:

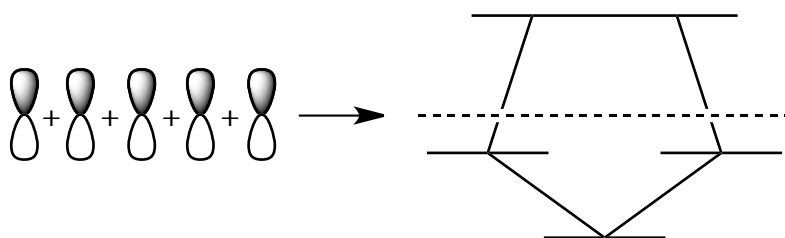
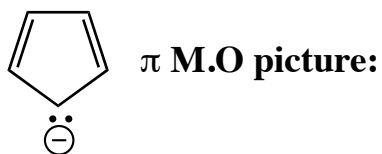


Look @ the M.O. picture for cyclopentadiene and the cyclopentadienyl cation:



How many e-'s?

compare with:



How many e-'s?

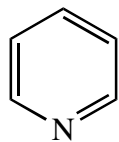
Heterocyclic compounds can also be aromatic:

Heteroatom: Any atom that is not C or H

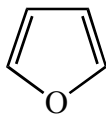
A Heterocycle: A cyclic compound with at least one ring atom that is not carbon.

Heterocycles can contain: N, O, S, P, Al, & Si

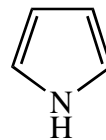
Determine which of following heterocycles are aromatic:



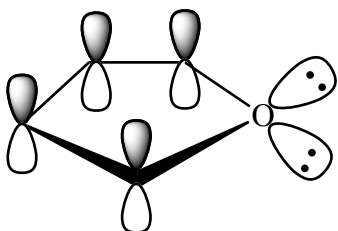
pyridine



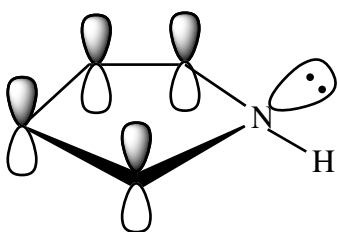
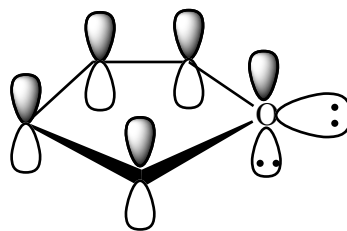
furan



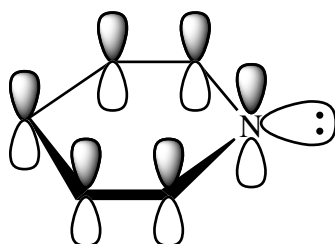
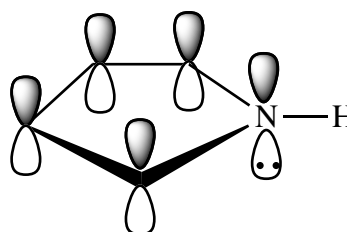
pyrrole



rehybridize →

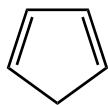


rehybridize →

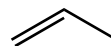


III. Some Chemical Consequences of Aromaticity

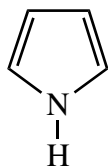
Some compounds are unusually acidic because their conjugate bases are aromatic. Other compounds are much less acidic than expected because deprotonation disrupts aromaticity. Cyclopentadiene, for example, is much more acidic than the similarly substituted acyclic compound:



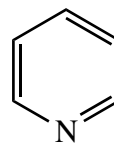
compare with:



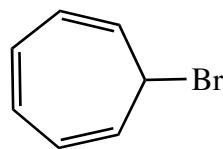
Heterocycles have interesting acid-base properties based upon the aromaticity of their conjugate acids/bases. Pyrrole, for example, is much less basic than pyridine:



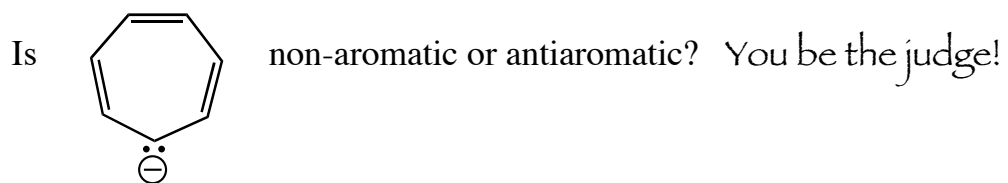
compare with:



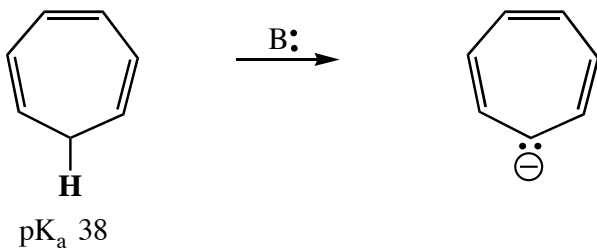
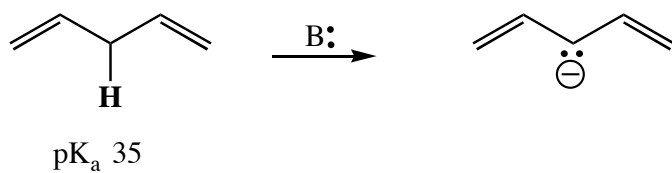
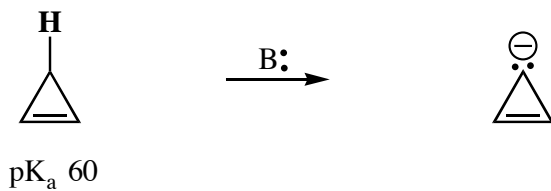
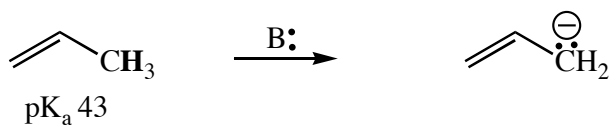
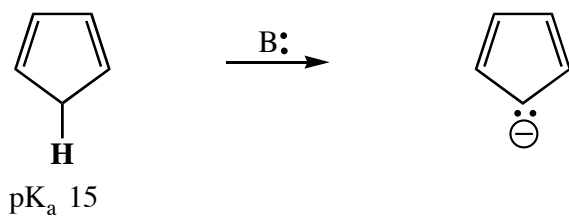
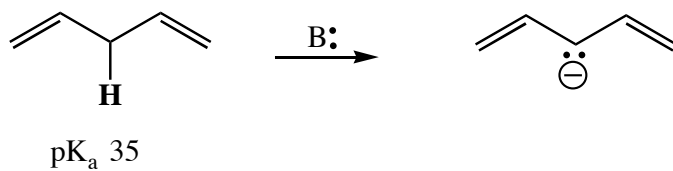
Another example of the influence of aromaticity on chemical reactivity is the unusual behavior of cycloheptatrienyl bromide:



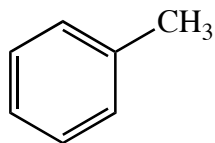
Challenge question:



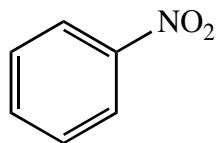
We can use pK_a's to estimate stability:



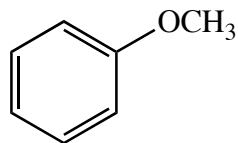
IV. Nomenclature:



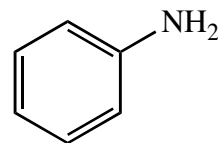
toluene



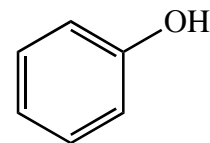
nitrobenzene



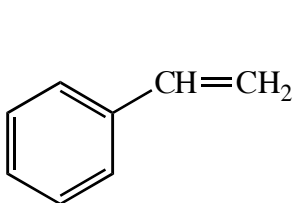
anisole



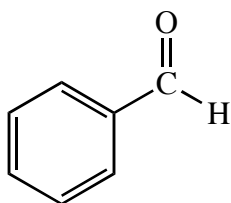
aniline



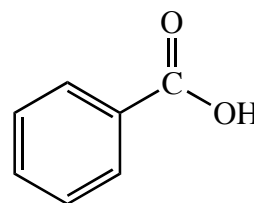
phenol



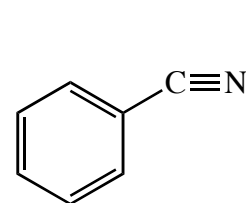
styrene



benzaldehyde

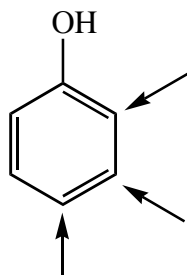


benzoic acid



benzonitrile

Can use *o*, *p*, *m*, or numbers when naming disubstituted aromatic rings.



- ☛ If one of the substituents can be incorporated into a name, the name is used, and that incorporated substituent is given the 1-position. If the benzene ring has **more than two** substituents, the substituents are numbered.

Examples:

